Supplementary Information

A Highly Efficient Colourless Sulphur/Iodide-based Hybrid Electrolyte for Dye-sensitized Solar Cells

Jiayan Cong,[a] Xichuan Yang,*[a] Yan Hao,[a] Lars Kloo[b] and Licheng Sun*[a,b]

[a] *State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), # Linggong Rd. 116024 Dalian, China;*
[b] *School of Chemical Science and Engineering, Center of Molecular Devices, Department of Chemistry, Royal Institute of Technology (KTH), Teknikringen 30, 10044 Stockholm, Sweden*

Synthesis of tetramethylammonium sulfide (TMAS):

A 25 wt.% solution of tetramethylammonium hydroxide in water (16.00 g, 44 mmol; Sinopharm Chemical Reagent Co., Ltd.) was added to a ammonium sulfide water solution with a concentration of 17 % (9.35 g, 22 mmol; Yizhong Chemical plant in Tianjin Dagang). The mixture was stirred and the water was evaporated and the resulting white solid was dried under vacuum at 40 ^{o}C.

Synthesis of the polysulfide (S^{2-}/S_x^{2-}) redox couple with tetramethylammonium cation:

Sulphur (40 mg, 1.25 mmol) and tetramethylammonium sulphide (TMAS, 225 mg, 1.25 mmol) were dissolved in 25 mL acetonitrile, and then heated at 70 ºC for 3 hours. The solution turned to green. Then put the solution in room temperature overnight, the solution turn to transparent and colorless. The solvent was diluted, and used in the electrolyte. To investigate the resultant, we repeat the experiment in ethanol, and we can get transparent crystal by recrystallisation. The elementary analysis was carried with the result (Found/% N: 9.019; C:

31.365; S: 52.015; H: 7.601; Calcd/% N: 9.077; C: 31.135; S: 51.950; H: 7.838), which leaded to the compound $[N(CH_4)_4^+]_2\ S_5^{2-}$.

Electrochemical characterization of the redox couple:

Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three electrode cell and an electrochemical workstation (BAS100B, USA). The working electrode was a glass carbon electrode (HCH Instruments, Inc., Part Number: MF-2012), the auxiliary electrode was a Pt wire (HCH Instruments, Inc., Part Number: CHI115), and Non-Aqueous Ag/Ag^+ reference (HCH Instruments, Inc., Part Number: CHI112) was used as reference electrode. Tetrabutylammonium hexaflourophosphate ($TBAPF_6$) 0.01 M was used as supporting electrolyte in CH_3CN. Usually, the ferrocenium/ferrocene (Fc^+/Fc) redox couple is used as an internal potential reference. Howerer, in our systems the redox couple can react with ferrocene, and instead we use the oxidizing potential of oxygen as the internal potential reference (green line in Fig. S3). CV experiments were carried out at 22 ^oC over the potential range 1.5 V to -1.5 V vs. Ag/Ag^+ at a scan rate of 100 mV s^{-1}.

Device fabrication:

TiO_2 film fabrication: Fluorine-doped tin oxide (FTO) glass plates (Pilkington-TEC8) were cleaned (in the order: detergent water solution, and ethanol) using an ultrasonic bath. A layer of compact TiO_2 was deposited on the conducting glass substrate by an electrochemical method. The deposition bath was an alkaline (pH = 10) aqueous solution (250 ml) containing 40 mmol titanium tetrachloride $TiCl_4$ (Aladdin Chemistry Co., Ltd., 99.9 %), 40 mmol ethylenediaminetetraacetic acid EDTA (China Harbin Chemical Reagent Plant, 99.5 %) and 25 mmol sodium chloride NaCl

(Tianjin Damao Chemical Reagent Factory, 99.5 %). The depositions were performed at room temperature (22 ºC) in a 250 ml beaker using a three-electrode configuration. The substrate was a 25×75 mm FTO substrate film previously cleaned by ultrasonic washing. A platinum wire electrode (HCH Instruments, Inc., Part Number: CHI115) served as the counter electrode and an Ag/AgCl electrode (HCH Instruments, Inc., Part Number: CHI111) was used as the reference. The deposition potential was -0.8 V vs. Ag/AgCl, and deposition time was set to 30 min. An electrochemical workstation (Shanghai Huachen Instruments, model CH1630D) interfaced with a PC was employed for the depositions. A layer of 13 nm (DHS-TPP3, Heptachroma, China) paste (ca. 2.4 μm) was coated on the deposited FTO glass by screen printing and then dried for 6 min at 125 ^{o}C. This procedure was repeated for 5 times (ca. 12 μm) and 8 times (ca. 19 μm) respectively. Thereafter, a layer of 300 nm (DHS-SLP1, Heptachroma, China) titania paste (ca. 4 μm) was coated as scattering layer. The double-layer TiO_2 electrodes (area: 6×6 mm) were gradually heated under an air flow at 520 °C for 30 min. The sintered film was further treated with 40 mM $TiCl_4$ aqueous solution at 70 ºC for 30 min, then washed with water and ethanol, and annealed at 500 ºC for 60 min. After the film was cooled to 80 °C, it was immersed into a 2×10^{-4} M dye solution of cis-bis(isothiocyanato)bis(2,2"-bipyridyl-4,4"-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (N719) solution in ethanol and maintained under dark conditions for 24 h. The sensitized TiO_2 electrode was then rinsed with ethanol and dried. The hermetically sealed cells were fabricated by assembling the dye-loaded film as the working electrode and a sputtered Pt/FTO counter electrode separated with a hot-melt Surlyn 1702 film (25 μm, Dupont).

The explanation of peaks in the cyclic voltammograms:

In order to investigate the electron transport process in the electrolytes, several compositons of the electrolytes were investigated by cyclic voltammetry (CV). As shown in Fig. S1, a solution of 0.01 M I_2 was studied as reference. Only one oxidation peak was found in the range from 0 to 1000 mV, and it is supposed to correspond to the oxidation of I_2/I_3^-. When an excess of LiI (0.03 M) is added to the solution, the single oxidation peak splits into two peaks (Fig. S2). The left one corresponds to the oxidation of I_2/I_3^- and the right one to the oxidation of I^-/I_3^-. This is similar to the shape of the CV curve for the hybrid electrolyte **C** (red curve in Fig. S3) mentioned in the main article. (Electrolyte **A** contains the redox system S^{2-}/S_x^{2-} only the electrolyte **B** corresponds to the hybrid electrolyte and electrolyte **C** corresponds to electrolyte A with an excess of I_2.)

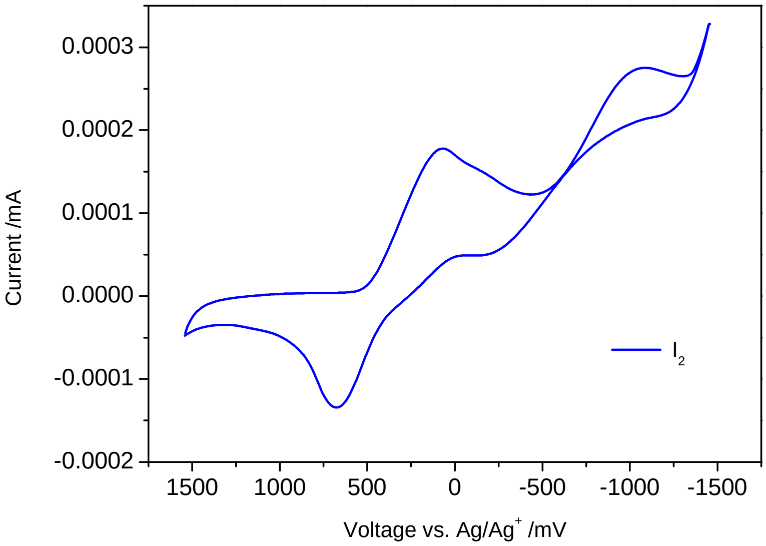

Fig. S1 CV-curve of the iodine in acetonitrile solution. The working electrode was a glassy carbon electrode, the auxiliary electrode was a Pt wire, and a non-aqueous Ag/Ag^+ electrode was used as reference electrode. Tetrabutylammonium hexaflourophosphate ($TBAPF_6$) of 0.01 M concentration was used as supporting electrolyte in acetonitrile.

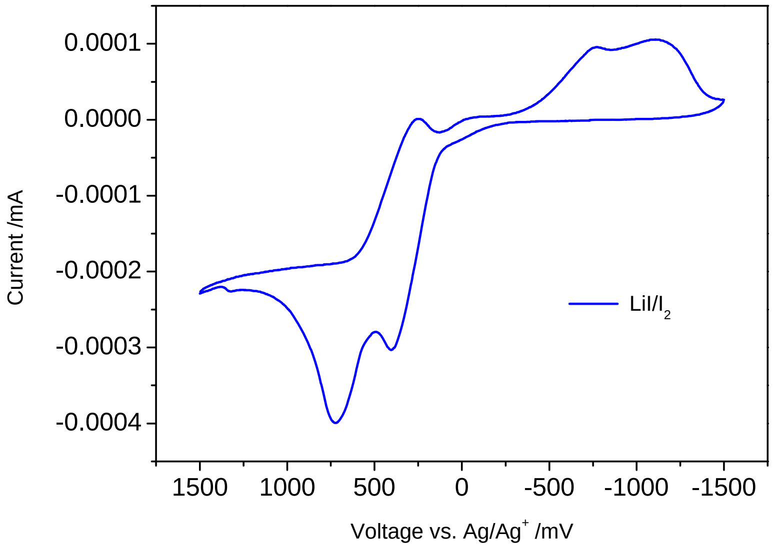

Fig. S2 CV-curve of the LiI/I$_2$ in acetonitrile solution. The working electrode was a glassy carbon electrode, the auxiliary electrode was a Pt wire, and a non-aqueous Ag/Ag$^+$ electrode was used as reference electrode. Tetrabutylammonium hexaflourophosphate (TBAPF$_6$) of 0.01 M concentration was used as supporting electrolyte in acetonitrile.

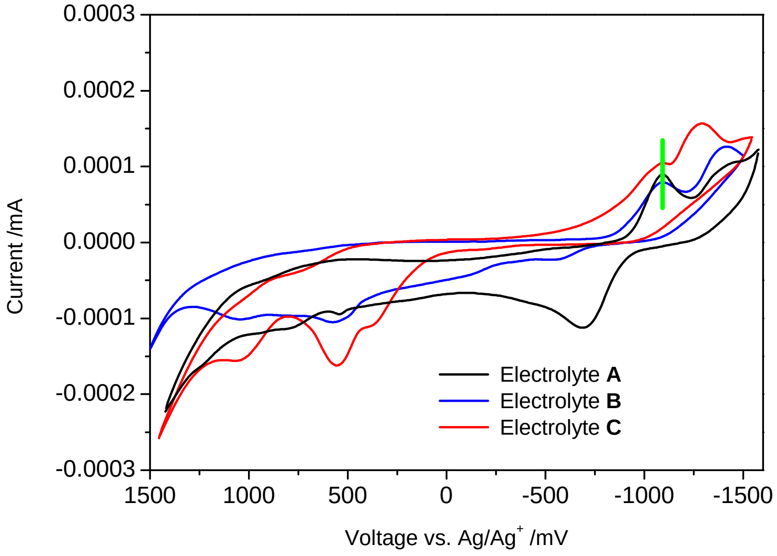

Fig. S3 CV-curve of the electrolytes A-C in acetonitrile solution. The working electrode was a glassy carbon electrode, the auxiliary electrode was a Pt wire, and a non-aqueous Ag/Ag$^+$ electrode was used as reference electrode. Tetrabutylammonium hexaflourophosphate (TBAPF$_6$) of 0.01 M concentration was used as supporting electrolyte in acetonitrile.

The equivalent circuit model of EIS:

The EIS spectra were measured under AM 1.5 illumination at V_{oc}, at room temperature. The equivalent circuit model is shown in Fig S4. A series resistance (R_s) was introduced to describe the ohmic resistance of the load and the conducting substrate. Recombination resistance at the TiO_2/electrolyte interface and the chemical capacitance of the TiO_2 were described by R_r and C_μ. The counter-electrode charge transfer resistance (R_{CE}) the associated C_{CE} were measured by fitting the arc observed at higher frequencies in Fig. 6. The impedance of diffusion in the electrolyte is described by Warburg impedance (Z_W).

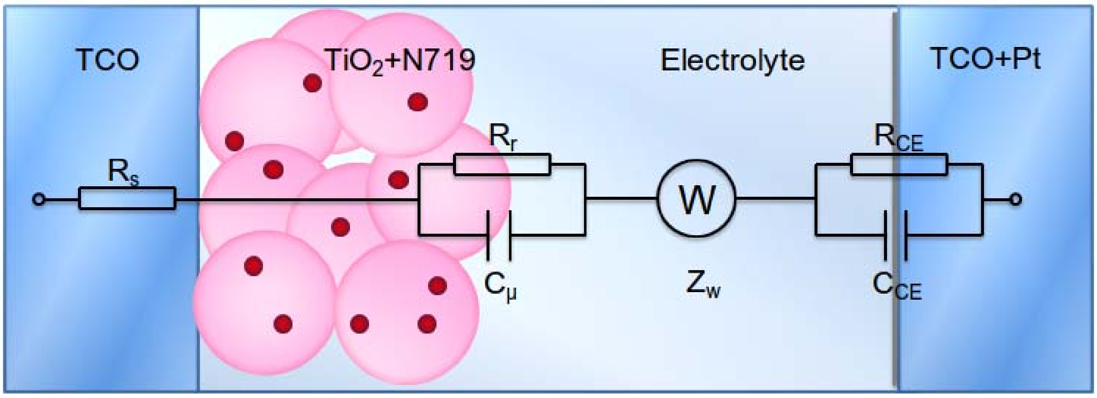

Fig. S4 Equivalent circuit model to fit the experiment data.

Measurement of conduction band edge of TiO_2 in different electrolytes:

Mott-Schottky plot were used to estimate the conduction band edge of TiO_2. Mott-Schottky plots were measured in three electrodes system by Electrochemical workstation (Zahner). The result are shown in Fig. S5. The working electrode was double layer TiO_2 film that used in fabrication of DSCs, the counter electrode was a Pt wire, and 0.1 M Ag/$AgNO_3$ reference was used as reference electrode. The hybrid electrolyte **SI4** and conventional iodine/triiodine electrolyte **I1** was measured. Calculated from the Mott-Schottky plots, the conduction band of

TiO_2 using hybrid electrolyte is about 20 mV negative than the conventional iodide/triiiodide electrolyte.

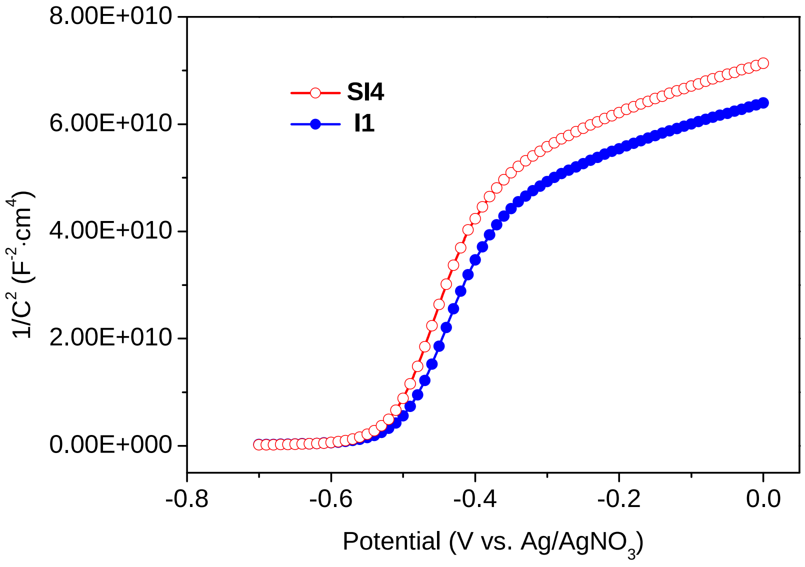

Fig. S5 Mott-Schottky plots of TiO_2 in hybrid electrolyte SI4 (open symbols) and conventional iodine/iodide electrolyte I1 (filled symbols).

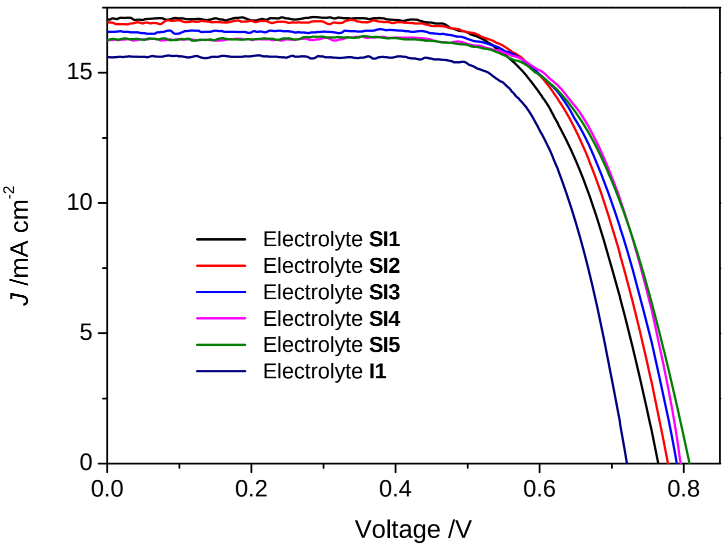

Fig. S6 Photocurrent density-voltage curves (*J*-*V*) of DSCs containing a hybrid or an iodine-based redox electrolyte. Data are shown for DSCs containing the hybrid electrolyte **SI** series and the pure I^-/I_3^-based electrolyte **I2**. Electrolytes **SI1** to **SI5**: contain different amount of TMAS and the other solutes: 0.60 M DMPII, 0.28 M TBP, 0.068 M LiI, 0.05 M GuSCN; electrolyte **I1**: 0.60 M DMPII, 0.03 M I_2, 0.053 M LiI, 0.28 M TBP and 0.05 M GuSCN; electrolyte: **I2** 0.60 M DMPII, 0.03 M I_2, 0.068 M LiI, 0.28 M TBP and 0.05 M

GuSCN, all the electrolytes were based on acetonitrile as solvent. The cells were investigated under air mass 1.5 global (AM 1.5 G) (100 mW·cm^{-2}) light irradiation.

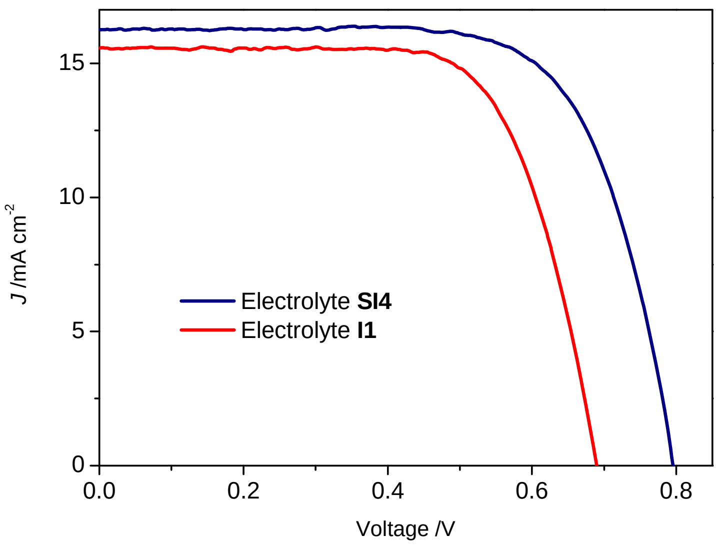

Fig. S7 Photocurrent density-voltage curves (*J*-*V*) of devices for electrochemical impedance investigation. Devices contained 19 + 4 μm double-layer TiO_2 film. Hybrid electrolyte **SI4** (0.20 M TMAS, 0.20 M S, 0.60 M DMPII, 0.28 M TBP, 0.068 M LiI, 0.05 M GuSCN), and the I^-/I_3^--based electrolyte **I1** (0.60 M DMPII, 0.03 M I_2, 0.053 M LiI, 0.28 M TBP and 0.05 M GuSCN) were used. Cells were investigated using a metal mask with an aperture area of 0.159 cm^2 and under air mass 1.5 global (AM 1.5 G) (100 mW·cm^{-2}).

Table S1 Photovoltaic characteristics of devices used for electrochemical impedance investigation.

	V_{oc} (mV)	J_{sc} (mA·cm^{-2})	*FF*	η (%)
SI4	796	16.3	0.70	9.1
I1	690	15.6	0.70	7.5

Detailed photovoltaic parameters of devices for electrochemical impedance investigation under AM 1.5 G irradiation.

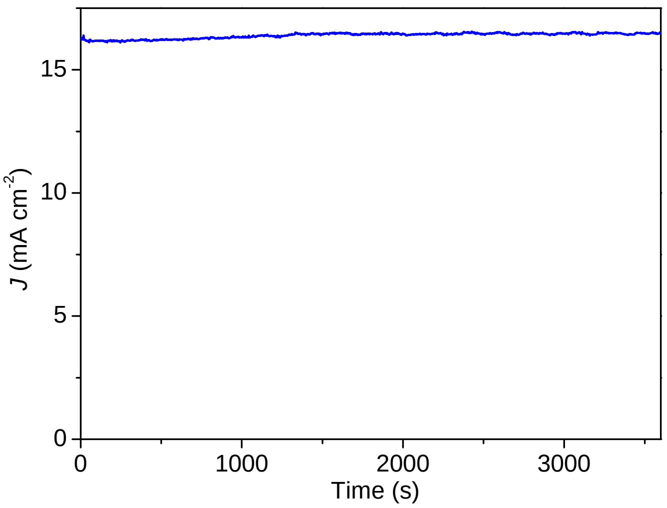

Fig. S8 The current density-time curve of DSC based on the electrolyte SI4 during 1 hour of light irradiation.